Primary Processes in the Flash Photolysis of Dimethyl Carbonate Vapor II: Discrimination of the Hydrogen Producing Primary Processes (Commemoration Issue Dedicated to Professor Rempei Gotoh On the Occasion of his Retirement)

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Primary Processes in the Flash Photolysis of Dimethyl Carbonate Vapor II

Discrimination of the Hydrogen Producing Primary Processes

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In succession to the previous paper on the primary steps of direct photolysis of dimethyl carbonate vapor by flash method (1849 A) at room temperature, in which the details of the hydrogen producing processes could not be elucidated, further investigation has been made with the intention to discriminate hydrogen formation processes.

From the isotopic compositions of hydrogen from the mixtures of $(CH_3O)_2CO$—$(CD_3O)_2CO$, measured mass-spectrometricaly, it has been shown that about 32% of the produced hydrogen is formed intramolecularly. The following hydrogen producing primary processes explain the isotopic distribution of hydrogen reasonably :

$$\begin{aligned} (CH_3O)_2CO+h\nu &\longrightarrow 3CO+3H_2, \\ &\longrightarrow 3CO+2H_2+2H, \quad 25\sim50\% \\ &\longrightarrow 3CO+H_2+4H. \quad 75\sim50\% \end{aligned}$$

INTRODUCTION

In the previous paper,[1] we proposed the following primary steps in the flash photolysis of dimethyl carbonate (DMC) vapor at 1849 A on the basis of the product analyses :

$$\begin{aligned} (CH_3O)_2CO+h\nu &\longrightarrow CH_3O+CH_3+CO_2, \quad 51\% \\ &\longrightarrow CH_4+CH_2O+CO_2, \quad 9\% \\ &\longrightarrow 3CO+3H_2 \text{ (over-all)}. \quad 40\% \end{aligned}$$

However, it has not been clear whether the hydrogen is produced as an atom or through intramolecular elimination in the primary steps. The photolysis of $(CH_3O)_2CO$—$(CD_3O)_2CO$ mixtures must reveal this matter, *i.e.*, the existence of only H_2 and D_2 will be a proof that hydrogen is formed by intramolecular elimination, and on the other hand the presence of an appreciable amount of HD will reflect the atom formation in the system. Thus the isotopic composition measurement of hydrogen has been conducted on the flash photolysis of $(CH_3O)_2CO$—$(CD_3O)_2CO$ mixtures, the results of which is presented in this paper.

EXPERIMENTALS

The apparatus, reaction system and optical arrangement were essentially

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identical with those described previously.[1] Three hydrogen isotopes, H_2, HD and D_2 were analysed quantitatively by means of CEC Model 21-401 mass-spectrometer, where the average value of the sensitivities of H_2 and D_2 was adopted as the sensitivity of HD.

Dimethyl carbonate was purified by repeated bulb-to-bulb distillation. Gas chromatogram showed no impurity.

Dimethyl carbonate-d_6 was prepared[2~4] by passing 0.3 mole of carbonyl chloride into 0.25 mole of boiling methanol-d_4 (E. Merk A. G. Darmstadt, Germany. 99 atomic %). After addition of 0.1 mole of methanol-d_4 and reflux for 10 hours in order to convert methyl chloroformate-d_3 produced as a by-product into dimethyl carbonate-d_6, the products were fractionally distilled. Distillate in the boiling range of 89.0~90.0°C was futher purified by repeated bulb-to-bulb distillation under vacuum. No impurity was detected by gas chromatography with a flame ionization detector.

Since the amounts of H_2 and/or HD formed from partially deuterated dimethyl carbonate in the prepared dimethyl carbonate can be obtained as the ratio to the amount of D_2 in the flash photolysis of that sample alone, mass-spectrometric purity test of the prepared dimethyl carbonate-d_6 was not performed.

RESULTS AND DISCUSSION

The results are summarized in Table 1 and Fig. 1. As may be seen from the isotopic analyses, the hydrogen formed in the flash photolysis is rich in the unmixed ones, though some HD were detected. And as shown in the last column, there is a large deviation of the value of $[HD]^2/[H_2][D_2]$ from the equilibrium constant for H_2-D_2 system, *i.e.*, 3.25 at 25°C[5].

Table 1. Hydrogen Isotope Analyses in the Flash photolysis of $(CH_3O)_2CO$—$(CD_3O)_2CO$ Mixtures.

$\frac{[DMC]}{[DMC\text{-}d_6]}$	Total Press. (mm Hg)	H_2	HD (mole %)	D_2	$\frac{[HD]^2}{[H_2][D_2]}$
0	22.7	0	8.25	91.75	
0.228	24.5	16.4	27.9*	55.7	0.92
0.580	24.0	33.3	34.7*	32.0	1.06
1.00	21.0	45.4	33.7*	20.9	1.09
2.08	23.0	64.6	25.5*	9.9	1.00
3.04	24.1	73.0	20.6*	6.4	0.95
3.94	24.8	76.6	18.0*	5.4	0.89

* As the HD was produced 0.09 relative to D_2=1.00 in the products of the photolysis of the prepared DMC-d_6 alone, the HD from the partialy deuterated dimethyl carbonate was corrected by subtracting 9% of D_2 from the observed amounts of the HD in other runs.

This can be interpreted most simply in terms of the formation of both hydrogen atom and molecule in our system. Since HD should be formed intermolecularly in the succeeding steps and H_2 and D_2 can result from both inter- and intramolecular reactions, it may be natural to assume that hydrogen is

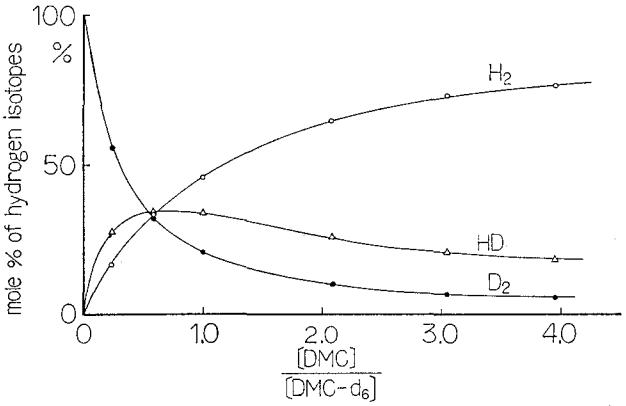

Fig. 1. Variation of the yields of hydrogen isotopes with [DMC]/[DMC-d_6].

formed partly by molecular detachment and partly as an atom in the primary process, *i.e.*,

$$(CH_3O)_2CO+h\nu \longrightarrow 3CO+aH_2+bH,$$

where $2a+b=6$, from a stoichiometric relation.

There can be two sources of HD: (1) D or H atom abstraction by H or D atom from dimethly carbonate-d_6 or dimethyl carbonate, respectively, and (2) recombination reaction of H and D atoms.

The hydrogen isotope production may be represented by the following reaction mechanism:

$$(CH_3O)_2CO+h\nu \longrightarrow 3CO+aH_2+bH, \quad \varepsilon_H[DMC] \tag{I}$$
$$(CD_3O)_2CO+h\nu \longrightarrow 3CO+aD_2+bD, \quad \varepsilon_D[DMC\text{-}d_6] \tag{II}$$
$$H+(CH_3O)_2CO \longrightarrow H_2+CH_3OCO_2CH_2, \quad k_1 \tag{1}$$
$$H+(CD_3O)_2CO \longrightarrow HD+CD_3OCO_2CD_2, \quad k_2 \tag{2}$$
$$D+(CD_3O)_2CO \longrightarrow D_2+CD_3OCO_2CD_2, \quad k_3 \tag{3}$$
$$D+(CH_3O)_2CO \longrightarrow HD+CH_3OCO_2CH_2, \quad k_4 \tag{4}$$
$$H+H+M \longrightarrow H_2+M, \quad k_5 \tag{5}$$
$$H+D+M \longrightarrow HD+M, \quad k_6 \tag{6}$$
$$D+D+M \longrightarrow D_2+M, \quad k_7 \tag{7}$$

where ε_H or ε_D is the absorption coefficient of ordinary dimethyl carbonate or deutrated dimethyl carbonate, respectively, and parentheses represent the concentration of the compound. M is DMC and/or DMC-d_6, and k's are rate constants.

Reaction (5)~(7) may be excluded from the following conciderations.

The values of rate constants in the above scheme are not available, but k_1 may be roughly estimated as follows.

The rate constants of next reactions (8)~(10) are known:

$$H+C_2H_6 \longrightarrow H_2+C_2H_5 \tag{8}$$
$$CD_3+C_2H_6 \longrightarrow CD_3H+C_2H_5, \tag{9}$$
$$CD_3+CH_3OH \longrightarrow CD_3H+CH_2OH, \tag{10}$$
$$H+CH_3OH \longrightarrow H_2+CH_2OH. \tag{11}$$

$\log_{10}(k_8/1\ \text{mole}^{-1}\ \text{sec}^{-1})=9.53-6800/2.303RT$,[6]

$$\log_{10}(k_9/1\ \text{mole}^{-1}\ \text{sec}^{-1}) = 7.628 + 1/2 \log T - 11300/2.303RT,^{7)}$$
$$\log_{10}(k_{10}/1\ \text{mole}^{-1}\ \text{sec}^{-1}) = 7.38 - 8140/2.303RT.^{8)}$$

If we assume that the ratio of the rates of abstraction of H from ethane and from methanol is the same for hydrogen atom and methyl-d_3 radical, we get $k_{11} = k_8 k_{10}/k_9 = 2.16 \times 10^5$ 1 mole^{-1} sec^{-1} at 300°K. Further if the rate of hydrogen abstraction from methoxy group of dimethyl carbonate is equal to that of methanol, we obtain $k_1 = k_{11}$.

Now, the rate constant of reaction (5) for M=DMC, though not available, must be of the order of 3×10^{10} l^2 mole^{-2} sec^{-1} by analogy to the value obtained for water as the third body.[9] Then the relative rate of reaction (5) to (1), R_5/R_1, is $k_5(\text{H})/k_1$.

The concentration of hydrogen atom should be much less than 7×10^{-7} atom /l/flash because the decomposition is lower than 5%, then we have $R_5/R_1 \ll 0.1$. This means that the extent of recombination reactions, (5)~(7), must be, if not at all, much less than 10% in the hydrogen producing steps.

Moreover, if reaction (I), (II) and (5)~(7) are predominant sources of hydrogen isotopes, the following relation can be deduced under steady-state condition:

$$\frac{R(\text{H}_2)R(\text{D}_2)}{R(\text{HD})^2} = \frac{a}{b} \cdot \frac{R(\text{H}_2)+R(\text{D}_2)}{R(\text{HD})} + \text{constant},$$

where constant is equal to $\frac{1}{K_e} \cdot \left(2\frac{a}{b}+1\right)^2 - \left(\frac{a}{b}\right)^2$ and K_e is a equilibrium constant for H_2-D_2 system.

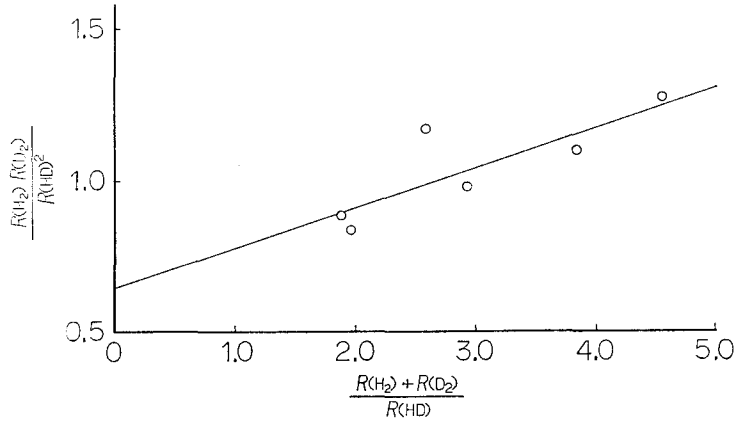

Fig. 2. Plot of $R(\text{H}_2)R(\text{D}_2)/R(\text{HD})^2$ against $(R(\text{H}_2)+R(\text{D}_2))/R(\text{HD})$.

When our experimental data are plotted in the form given by this equation, we obtain that a/b is equal to 0.13 from the gradient, and the "constant" is 0.646 (see Fig. 2), accordingly K_e becomes 2.42. This value deviates largely from the equilibrium constant, 3.25 at 25°C and 3.18 even at 0°C,[5] suggesting that the atom recombination is not the major process. Therefore, reactions (5) ~(7) may be omitted in the above reaction scheme, and the hydrogen isotopes must result from reaction (I), (II) and (1)~(4).

Now, assuming steady-state behavior we get the following rate relation:

$$\frac{R(H_2)}{R(D_2)}=\frac{\varepsilon_H}{\varepsilon_D}\cdot X\cdot\frac{a+\dfrac{b\alpha X}{1+\alpha X}}{a+\dfrac{b}{1+\alpha X}}, \tag{A}$$

where X represents the ratio of [DMC]/[DMC-d_6], and only primary isotope effect is assumed *i.e.*, that $k_1/k_2=k_4/k_3=\alpha$.[8,10~12]

The values of α and $\varepsilon_H/\varepsilon_D$ are not available, but since α is a constant, mathematically there must exist the unique value of X which satisfies $\alpha X=1$. For the value of $X=1/\alpha$, eq. (A) is rewritten in the following form:

$$\frac{\varepsilon_H}{\varepsilon_D}=\alpha\frac{R(H_2)}{R(D_2)}. \tag{B}$$

Thus, assuming any certain value α_0, we can fix the corresponding single value, $X_0=1/\alpha_0$ from Fig. 1, and the ratio of absorption coefficients, $\varepsilon_H/\varepsilon_D$, is obtained by inserting the assumed α_0 and the observed value of $(R(H_2)/R(D_2))_0$ into eq. (B).

On the other hand, we have

$$\frac{R(H_2)+R(D_2)}{R(HD)}=\left(1+\frac{a}{b}\right)\left(\frac{\alpha X}{1+\varepsilon_D/\varepsilon_H}+\frac{1}{1+\varepsilon_H/\varepsilon_D}\cdot\frac{1}{X}\right)+\frac{a}{b}. \tag{C}$$

Using assumed α_0 and the value of $\varepsilon_H/\varepsilon_D$ obtained from eq. (B), we can get the value of a/b from both gradient and intercept in eq. (C). Then α_0 can be estimated by trial and error method until the values derived by both procedures

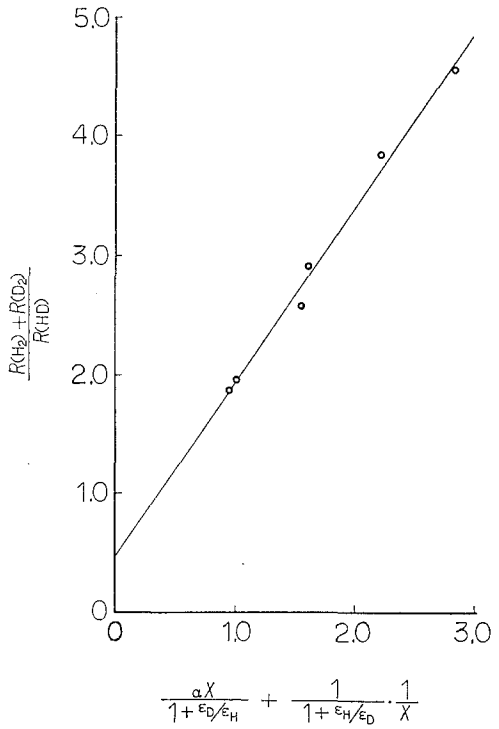

Fig. 3. Plot of $(R(H_2)+R(D_2))/R(HD)$ against $\left\{\frac{\alpha X}{1+\varepsilon_D/\varepsilon_H}+\frac{1}{1+\varepsilon_H/\varepsilon_D}\cdot\frac{1}{X}\right\}$.

coinside. Such value of α_0 is found to be 1.02, and $\varepsilon_H/\varepsilon_D$ and a/b are 2.14 and 0.48, respectively. This means that the fraction of the total hydrogen formed molecularly is about $0.48/(1+0.48)=0.32$, because one hydrogen atom forms one hydrogen molecule in the above scheme.

From $2a+b=6$ and $a/b=0.48$ we have $(CH_3O)_2CO+h\nu \longrightarrow 3CO+3/2H_2+3H$, as an apparent stoichiometric relation, but actually the following primary processes must be involved :

$$(CH_3O)_2CO+h\nu \longrightarrow 3CO+3H_2, \qquad p \qquad (12)$$
$$\longrightarrow 3CO+2H_2+2H, \qquad q \qquad (13)$$
$$\longrightarrow 3CO+H_2+4H, \qquad r \qquad (14)$$

where p, q and r are the respective probabilities with which reactions (12), (13) and (14) occur, and other hydrogen atom producing steps can be ruled out from the energetic considerations.

Since $p+q+r=1$ and $a/b=(3p+2q+r)/(2q+4r)\simeq 1/2$, we get $p=r-1/2$ and $q=3/2-r$. Since p and q can not be negative, we obtain $3/4\geq r\geq 1/2$.

We have estimated that the hydrogen producing primary processes amount to 40% of all primary steps,[1] then the extent of the reaction (14) becomes to be from 20 to 30%.

Since dimethyl carbonate vapor absorbs the light shorter than 2,000 A,[13] the 1849 A line lies near the threshold of absorption of dimethyl cabonate. Then it may not be unreasonable that $\varepsilon_H/\varepsilon_D$ has the value 2.14 at 1849 A, as is supposed from the instances that the absorption coefficients of the deutrated hydrocarbons are about one half of that of the ordinary ones near the threshold of its absorption.[14~17]

CONCLUSION

From the results in the previous paper[1] and the hydrogen isotopic composition of the hydrogen from the mixtures of $(CH_3O)_2CO$—$(CD_3O)_2CO$, the fraction of the hydrogen formed molecularly is about 0.32 of the total hydrogen, and in the flash photolysis of dimethyl carbonate vapor the following primary processes can explain the observed reaction products and the isotopic distribution in the hydrogen :

$$(CH_3O)_2CO+h\nu \longrightarrow CH_3+CH_3O+CO_2, \qquad 51\%$$
$$\longrightarrow CH_4+CH_2O+CO_2, \qquad 9\%$$
$$\left.\begin{array}{l}\longrightarrow 3CO+3H_2,\\ \longrightarrow 3CO+2H_2+2H,\end{array}\right\} \qquad 20\sim 10\%$$
$$\longrightarrow 3CO+H_2+4H. \qquad 20\sim 30\%$$

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REFERENCES

(1) T. Ibuki and Y. Takezaki, *this Bulletin*, **45**, 406 (1967).
(2) E. Muller, "Methoden der Organischen Chemie", Vol. 8, Georg Thieme Verlag, Stuttgart, 1952, p. 106.
(3) F. D. Chattaway and E. Saerens, *J. Chem. Soc.*, 708 (1920).
(4) H. Lux, *Chem. Ber.*, **62**, 1824 (1929).
(5) H. C. Urey, *J. Chem, Soc.* 562 (1947).
(6) M. R. Berlie and D. J. LeRoy, *Disc. Faraday Soc.*, **14**, 50 (1953).
(7) (a) J. R. McNesby and A. S. Gordon, *J. Am. Chem. Soc.*, **77**, 4719 (1955). (b) M. H. J. Wijnen, *J. Chem. Phys.*, **23**, 1357 (1955).
(8) R. Shaw and J. C. J. Thynne, *Trans. Faraday Soc.*, **62**, 104 (1966).
(9) W. Steiner, *ibid.*, **31**, 962 (1935).
(10) W. M. Jackson, J. R. McNesby, and B. de B. Darwent, *J. Chem. Phys.*, **37**, 1610 (1962).
(11) P. Gray and A. A. Herod, *Trans. Faraday Soc.*, **64**, 1568 (1968).
(12) P. Gray, A. Jones, and J. C. J. Thynne, *ibid.*, **61**, 474 (1965).
(13) A. S. Gordon and W. P. Norrish, *J. Phys. Chem.*, **69**, 3013 (1965).
(14) H. Okabe and D. A. Becker, *J. Chem. Phys.*, **39**, 2549 (1963).
(15) H. Okabe and J. R. McNesby, *ibid.*, **37**, 1340 (1962).
(16) C. L. Currie, H. Okabe, and J. R. McNesby, *J. Phys. Chem.*, **67**, 1494 (1963).
(17) P. G. Wilkinson and R. S. Mulliken, *J. Chem. Phys.*, **23**, 1895 (1955).